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## EFFECT OF PACKING IRREGULARITIES ALONG THE BED LENGTH

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### SUMMARY

Irregular variations of the void fraction (porosity),  $\varepsilon$ , and the column volume fraction taken up by the sorbent stationary phase,  $\mu$ , along the column length (packing irregularities) are shown to result in an additional sample peak dispersion (broadening). This effect is considered in detail in the framework of the theory of linear ideal sorption dynamics. An expression for the peak shape is also obtained for the general case of non-linear non-ideal sorption dynamics based on the concept of retardation time. In this case the packing irregularity is responsible for two effects: dispersion which combines additively with broadening caused by the usual non-ideality effect (kinetics of mass exchange), and a small peak asymmetry even for a linear isotherm. It is shown that the packing irregularity can be taken into account by adding a term to the retardation time and, an explicit expression for that term is obtained. Estimates show that, for a random packing of spheres, the irregularity-induced dispersion may be as much as several tens of per cent of the total effective peak dispersion and increases with decreasing packing particle size.

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### INTRODUCTION

The longitudinal dispersion of solute peaks transported through irregularly packed beds of granular particles of sorbent by a carrier gas is of major importance in adsorbers, catalytic reactors and chromatographic columns. In studies of the sorption dynamics in homogeneously packed beds the void fraction,  $\varepsilon$ , and the fraction of the column space taken up by the sorbent,  $\mu$ , are usually regarded as constants. However, for a model comprising random packing of spheres the value of  $\varepsilon$  has been shown (see, e.g., refs. 1 and 2) to vary irregularly along the bed length. This phenomenon has also been studied experimentally<sup>2</sup> (see also ref. 3 and references cited in refs. 1, 2). Even though the particles were large in all these experiments, the geometrical scaling of packing with particles of different sizes makes it possible to extend the results to the smaller particles which are generally used for chromatography.

The packing characteristics  $\varepsilon$  and  $\mu$  are not completely independent of each other:  $\mu$  increases with the packing density and with decreasing  $\varepsilon$ . Consequently, variations of  $\varepsilon$  along the bed length should result in associated variations in  $\mu$ . In the

case of solid adsorbents,  $\mu$  corresponds to the entire volume taken up by the particles, therefore  $\mu = 1 - \varepsilon$ . In gas-liquid chromatography the stationary phase is loaded on a solid support, filling its pores and comprising a fraction,  $m$ , of its weight

$$m = V_l \delta_l / V_s \delta_s$$

where  $V$  is the volume,  $\delta$  the density and the indices  $l$  and  $s$  denote the stationary phase and the solid support. If the sorbent phase is loaded perfectly uniformly, then  $m$  is the same for all the particles and:

$$\mu = (1 - \varepsilon) \cdot \frac{m \delta_s}{\delta_l} = (1 - \varepsilon) n$$

This relationship means that there is a linear dependence between  $\varepsilon$  and  $\mu$ .

In most cases, however, the stationary phase film covering the support surface is non-uniform and fills mainly randomly the narrow pores of the support; see refs. 1 and 4. Therefore,  $m$  may vary over a wide range from one particle to another, resulting in variations of  $\mu$  (with respect to its mean,  $\mu_0$ ) which are weakly connected with variations in  $\varepsilon$ . In this case  $\varepsilon$  and  $\mu$  can be regarded as independent quantities. We will show that irregularities in the packing and, consequently, in  $\varepsilon$  and  $\mu$ , along the length of the bed cause an additional peak dispersion both for linear and non-linear isotherms, regardless of whether  $\varepsilon$  and  $\mu$  are interdependent or independent.

## THEORETICAL

### *Effect of packing irregularity on linear ideal sorption dynamics in chromatography*

Let  $\Omega$  be a set of various realizations (*cf.*, ref. 5) of the bed packing, the porosity,  $\varepsilon_\omega(x)$ , and the column volume fraction occupied by sorbent,  $\mu_\omega(x)$ , where  $\omega \in \Omega$ , are random (stochastic) processes ( $x$  being a space coordinate along the bed) because normally the packing is highly irregular. Since the structure of a packed bed of section  $x_1$  is the same as that of section  $x_2$  (packing homogeneity), the random quantities  $\varepsilon_\omega(x_1)$  and  $\varepsilon_\omega(x_2)$  have the same probability distribution density. Then it follows that the distribution functions of the random quantities  $\varepsilon_\omega(x_1), \dots, \varepsilon_\omega(x_n)$  are invariant with respect to shifts along the coordinate  $x$ , or that the random process  $\varepsilon_\omega(x)$  is stationary. Moreover, from experimental observations<sup>2,3</sup>, this process can be considered as Gaussian. Similar reasoning can also be applied to the random process  $\mu_\omega(x)$  (for definitions see ref. 5, Ch. 2).

If  $\omega \in \Omega$  is a realization of the packing, then  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$  are realizations of the associated random processes. The evolution of a band in the theory of linear ideal sorption dynamics (chromatography) is described by

$$\varepsilon_\omega(x) \hat{c}_t C_\omega + \mu_\omega(x) \hat{c}_t a_\omega + w \hat{c}_x C_\omega = 0 \quad (1)$$

with boundary and initial conditions

$$C_\omega(x = 0, t) = f(t), \int_{-\infty}^{+\infty} dt f(t) = M < \infty \quad (2)$$

$$C_\omega(x, t = 0) = 0, 0 \leq x < \infty$$

where  $C(x, t)$  is the concentration of the solute in the mobile band and  $w$  is the carrier-gas flow velocity

$$w = u_\omega(x) \varepsilon_\omega(x) = \text{constant}$$

$u_\omega(x)$  being the linear flow velocity. Here  $f(t) \geq 0$  for  $t \geq 0$  corresponds to the inlet sample profile, and  $M$  is a total amount of the inlet sample.

Assuming that the isotherm is linear,  $a_\omega(x, t) = kC_\omega(x, t)$ , where  $k$  is a mass distribution coefficient, then:

$$[\varepsilon_\omega(x) + k\mu_\omega(x)] \partial_t C_\omega + w \partial_x C_\omega = 0 \quad (3)$$

Substituting in eqn. 3

$$x_\omega = x, t_\omega = t - \frac{1}{w} \int_0^x d\xi [\varepsilon_\omega(\xi) + k\mu_\omega(\xi)],$$

$$\tilde{C}_\omega[x_\omega(x, t), t_\omega(x, t)] = C_\omega(x, t) \quad (4)$$

where  $\xi$  is an integration variable, reduces it to a deterministic equation without stochastic coefficients:

$$w \partial_{x_\omega} \tilde{C}_\omega = 0 \quad (5)$$

$$\tilde{C}_\omega(x_\omega = 0, t_\omega) = C_\omega(x = 0, t) = f(t)$$

Because the processes are Gaussian and stationary, the quantities  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$  can be expressed in the form

$$\varepsilon_\omega(x) = \varepsilon_0 + \varepsilon_{1,\omega}(x), \mu_\omega(x) = \mu_0 + \mu_{1,\omega}(x) \quad (6)$$

where  $\varepsilon_0 = \langle \varepsilon_\omega(x) \rangle$  and  $\mu_0 = \langle \mu_\omega(x) \rangle$  are expectations (*i.e.*, mean values of random variables<sup>5</sup>) with respect to realizations  $\Omega$ , while  $\varepsilon_{1,\omega}(x)$  and  $\mu_{1,\omega}(x)$  are stationary Gaussian processes with zero means. The solution of eqns. 2 and 3 then has the form

$$C_\omega(x, t) = f \left[ t - \frac{\varepsilon_0 + k\mu_0}{w} \cdot x - \frac{v_\omega(x)}{w} \right] \quad (7)$$

where  $v_\omega(x) = \int_0^x d\xi [\varepsilon_{1,\omega}(\xi) + k\mu_{1,\omega}(\xi)]$  is also a random Gaussian process with a zero mean (non-stationary in a general case); ref. 5, Ch. 2.

Hence the solution  $C_\omega(x, t)$  of eqn. 3 for a fixed packing  $\omega$  is a function of the integral containing  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$ . Therefore, the eluted peak observed is influenced by the structure of the entire packing through which this peak has been propagated. Let us consider what this leads to.

Divide a column of length  $L$  into parts of length  $l$

$$r \ll l = x_{i=2n+1} - x_{i=2n} \ll L$$

where  $n = 1, 2, \dots$  and  $r$  is the mean radius of the packing particles; these parts are spaced at  $d \gg \lambda \approx r$ ,  $\lambda$  being the correlation length\* of the stochastic processes under consideration. The introduction of parameter  $d$  is dictated by the fact that the random quantities  $\varepsilon_\omega(x_1)$  and  $\varepsilon_\omega(x_2)$  are stochastically (randomly) correlated. The larger is  $\Delta x = x_2 - x_1$  the weaker is this correlation, and the bed packing structure is such that for  $\Delta x \gg \lambda$  the correlation can be regarded as having vanished. By virtue of the randomness and homogeneity of the packing, the random quantity  $\varepsilon_\omega(x)$  for  $x \in l_p = [x_{2p}, x_{2p+1}]$  depends on the value of  $\varepsilon_\omega(x)$  for  $x \in l_s$ , where  $s < p$ , and is independent of the values of the random quantity  $\varepsilon_\omega(x)$  when  $x \in l_q$  where  $q < s$ . To be more precise, for a conditional probability

$$\begin{aligned} \Pr [\varepsilon_\omega(x \in l_p) = y | \varepsilon_\omega(x' \in l_s) \in Y, \varepsilon_\omega(x \in l_{q_m}) \in X_m, \dots, \varepsilon_\omega(x \in l_{q_1}) \in X_1] \\ = \Pr \{ \varepsilon_\omega(x \in l_p) = y | \varepsilon_\omega(x' \in l_s) \in Y \} \equiv \mathbf{P}(x, y | x', Y) \end{aligned}$$

where  $\mathbf{P}(x, y | x', Y)$  is a transition-probability function\*\*. This property of a random process is known as the Markov property (ref. 5, Chs. 2 and 6). Note that a similar reasoning is applicable to  $\mu_\omega(x)$ . Therefore, the structure of the bed packing is such that random processes  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$  and also  $\varepsilon_{1,\omega}(x)$  and  $\mu_{1,\omega}(x)$  are Markovian and Gaussian.

Each segment  $l_p$  of length  $l$  can be regarded as a sub-realization of  $\omega \in \Omega$  which is independent of realizations on preceding segments  $l_{s < p-1}$ . Therefore, in travelling along the bed from  $x = 0$  to  $x = L$  the eluted peak is influenced by almost the whole set of realizations from  $\Omega$ , which results in self-averaging of the solution over the realizations  $\{\omega\} = \Omega$ . This implies that at the outlet of the column of length  $L \gg l$ , with probability 1 an observable peak  $C_\omega(x = L, t)$  coincides with the curve which is averaged over all realizations  $\Omega$ :  $C_\omega(L, t) = \langle C_\omega(L, t) \rangle$ . The self-averaging is confirmed also by the fact that for the variance of the random quantity  $C_\omega(x, t)$  one gets  $\mathcal{D}[C_\omega(x, t)] \approx x^{-1}$ . This implies that for  $x \rightarrow \infty$  with probability 1 we have (see ref. 6):

$$| C_\omega(x, t) - \langle C_\omega(x, t) \rangle | \rightarrow 0$$

Before averaging the solution 7 over all realizations  $\Omega$  let us find the probability distribution density for the random quantity  $v_\omega(x) = \int_0^x d\xi [\varepsilon_{1,\omega}(\xi) + k\mu_{1,\omega}(\xi)]$ . Because this process is Gaussian, it is dependent on two moments, the mean  $\langle v_\omega(x) \rangle$  and the variance  $\mathcal{D}[v_\omega(x)]$ . In our case  $\langle v_\omega(x) \rangle = 0$  while:

$$\begin{aligned} \mathcal{D}[v_\omega(x)] &= \langle v_\omega(x) v_\omega(x) \rangle \\ &= \int_0^x d\xi \int_0^x d\xi' \langle [\varepsilon_{1,\omega}(\xi) + k\mu_{1,\omega}(\xi)] [\varepsilon_{1,\omega}(\xi') + k\mu_{1,\omega}(\xi')] \rangle \end{aligned} \quad (8)$$

\* The correlation length of the stochastic process  $\xi_\omega(x)$  is usually defined as the scale of its decreasing covariance:  $\text{cov}(\xi_\omega(x_1), \xi_\omega(x_2)) \equiv \langle \xi_\omega(x_1) \xi_\omega(x_2) \rangle - \langle \xi_\omega(x_1) \rangle \langle \xi_\omega(x_2) \rangle \equiv \mathcal{R}(x_1 - x_2) \approx \exp(-|x_1 - x_2|/\lambda)$ .

\*\* The conditional probability  $\Pr \{ \varepsilon_\omega(x \in l_p) = y | \varepsilon_\omega(x' \in l_s) \in Y \}$  defines the function  $\mathbf{P}(x, y | x', Y) =$  probability that the random value  $\varepsilon_\omega(x') \in Y$  if for  $x < x'$   $\varepsilon_\omega(x)$  takes the value  $y$ . This function is usually called the transition-probability function.

By virtue of stationary nature of the process  $\varepsilon_{1,\omega}(x) + k\mu_{1,\omega}(x)$  we obtain

$$\langle [\varepsilon_{1,\omega}(\xi) + k\mu_{1,\omega}(\xi)] [\varepsilon_{1,\omega}(\xi') + k\mu_{1,\omega}(\xi')] \rangle = \mathcal{R}(\xi - \xi')$$

where  $\mathcal{R}(\xi - \xi')$  is a correlation function (covariance) whose rate of decrease is characterized in terms of the correlation length,  $\lambda$ . Because the process  $\varepsilon_{1,\omega}(x) + k\mu_{1,\omega}(x)$  is one-dimensional stationary, Gaussian and Markovian, the Doob theorem states that the correlation function  $\mathcal{R}(\xi - \xi')$ , where  $\xi$  and  $\xi'$  are real variables, has the following explicit form (see ref. 5, Ch. 5, paragraph 8)

$$\mathcal{R}(\xi - \xi') = D \cdot \exp\left(-\frac{|\xi - \xi'|}{\lambda}\right)$$

where  $D = \mathcal{R}(0) = \langle [\varepsilon_{1,\omega}(x) + k\mu_{1,\omega}(x)]^2 \rangle$ . Then from expression 8 it follows that the variance:

$$\begin{aligned} \mathcal{D}[v_\omega(x)] &= \int_0^x d\xi \int_0^x d\xi' \cdot \mathcal{R}(\xi - \xi') \\ &= 2D\lambda x + 2D\lambda^2 \cdot \exp(-x/\lambda) - 2D\lambda^2 \end{aligned}$$

For the case of  $x \gg \lambda$  we have  $\mathcal{D}[v_\omega(x)] = 2D\lambda x$ . This implies that the probability distribution density for the random quantity  $v_\omega(x)$  for  $x \gg \lambda$  has the form:

$$\mathcal{W}_v(\eta, x) = \frac{1}{\sqrt{2\pi D\lambda x}} \cdot \exp\left(-\frac{\eta^2}{2D\lambda x}\right) \quad (9)$$

Hence, using the expressions 7 and 9 we find that the solution of eqn. 3, with conditions 2, can be represented for  $L \gg \lambda$  by:

$$\begin{aligned} C_\omega(x = L, t) &\stackrel{\text{Prob}=1}{=} \langle C_\omega(x = L, t) \rangle \\ &= \int_{-x}^{+x} d\eta \cdot \mathcal{W}_v(\eta, x) \cdot f\left(t - \frac{\varepsilon_0 + k\mu_0}{w} \cdot x - \frac{\eta}{w}\right) \end{aligned} \quad (10)$$

It follows from eqn. 10 that the eluted peak changes its original profile  $f(t)$ , gradually becoming more and more dispersed. The dispersion disappears in the limit  $D\lambda x \rightarrow 0$ .

If the boundary condition 2 corresponds to a sharp concentration pulse, e.g., it is a delta-function  $f(t) = M\delta(t)$ , then from expression 10 for  $x \gg \lambda$ :

$$\langle C_\omega(x, t) \rangle = \frac{1}{\sqrt{2\pi D\lambda x}} \cdot M \cdot \exp\left[-\frac{\left(t - \frac{\varepsilon_0 + k\mu_0}{w} \cdot x\right)^2}{2D\lambda x}\right]$$

The latter relationship demonstrates that in this particular case the irregularity in packing along the length of the bed results in a zone broadening which takes the form of a Gaussian curve. Note that a solution of eqn. 3 with  $f(t) = M\delta(t)$  for constant coefficients  $\varepsilon(x) = \varepsilon_0$ ,  $\mu(x) = \mu_0$  is well known and corresponds to the stationary profile:

$$C(x, t) = M\delta\left(t - \frac{\varepsilon_0 + k\mu_0}{w} \cdot x\right)$$

From eqn. 10 we also find that the function  $\bar{C}(x, t) = \langle C_\omega(x, t) \rangle$  satisfies a new equation with a "diffusion-type" term on the right-hand side (see ref. 6):

$$(\varepsilon_0 + k\mu_0) \hat{c}_t \bar{C} + w \hat{c}_x \bar{C} = \frac{D\lambda}{2w} \cdot \hat{c}_t^2 \bar{C} \quad (11)$$

Eqn. 11 coincides with eqn. 3 for non-random coefficients  $\varepsilon_0$  and  $\mu_0$  because in this case  $D = 0$ . This means that the packing stochasticity (randomness) affects the sample peak evolution, when it travels through a bed, as some effective sorption kinetics. From eqn. 11 it follows that these kinetics correspond to the retardation-time concept for the description of adsorption-desorption kinetics (see final section, Appendix and refs. 7-9) with regard to the retardation-time value:

$$\tau^* = D\lambda/2wk\mu_0 \quad (12)$$

*Effect of packing irregularity for non-linear slightly curved sorption isotherm in non-ideal sorption dynamics*

The sorption dynamics equation in the framework of the retardation time concept (without packing irregularity) is well known and has the form

$$\varepsilon \hat{c}_t C + w \hat{c}_x C = -\mu \hat{c}_t a^* \quad (13)$$

where  $a^*(x, t)$  is the non-equilibrium concentration in the stationary phase which is regarded as at equilibrium for a time differing from a given time  $t$  by  $\tau$  (time of retardation), or  $a^*(x, t) = a(x, t - \tau)$ . Then, for a non-linear slightly curved isotherm in the case of a short retardation time,  $|k_2\tau \hat{c}_t C| \ll k_1$ , we obtain (see also Appendix):

$$a^*(x, t) = k_1 C(x, t - \tau) + k_2 C^2(x, t - \tau) \approx k_1 C(x, t) - \tau k_1 \hat{c}_t C + k_2 C^2(x, t)$$

Substituting this expression into eqn. 13 and allowing for the packing irregularity we get the non-linear equation with stochastic coefficients:

$$[\varepsilon_\omega(x) + k_1\mu_\omega(x)] \hat{c}_t C_\omega + w \hat{c}_x C_\omega + 2k_2\mu_\omega(x) C_\omega \hat{c}_t C_\omega = k_1\tau\mu_\omega(x) \hat{c}_t^2 C_\omega \quad (14)$$

Because  $\mu_\omega(x) \geq \mu_- > 0$  (where  $\mu_- \equiv \min \mu_\omega > 0$ ), after dividing both sides of eqn. 14 by  $\mu_\omega(x)$  and replacing the variables

$$x_\omega(x, t) = \frac{1}{w} \int_0^x d\zeta \cdot \mu_\omega(\zeta), \quad t_\omega(x, t) = t - \frac{1}{w} \int_0^x d\zeta \cdot \varepsilon_\omega(\zeta), \quad (15)$$

$$C_\omega(x, t) = C[x_\omega(x, t), t_\omega(x, t)]$$

we obtain the equation for the function  $C'(x_\omega, t_\omega)$

$$\hat{c}_{x_\omega} C' + k_1 \hat{c}_{t_\omega} C' + 2k_2 C' \hat{c}_{t_\omega} C' = k_1 \tau \hat{c}_{t_\omega}^2 C' \quad (16)$$

$$C'(x_\omega = 0, t_\omega) = f(t_\omega), \quad \int_{-x}^{+x} dt_\omega \cdot f(t_\omega) = M < \infty, \quad (16')$$

$$C'(x_\omega, t_\omega = 0) = 0$$

which unlike eqn. 14, does not contain stochastic coefficients  $\varepsilon_\omega(x)$  or  $\mu_\omega(x)$ . A general solution of expressions 16 and 16' has been given in ref. 8 where the important case of a rectangular sample profile has also been treated:

$$C'(x_\omega = 0, t_\omega) = \begin{cases} C_0, & 0 \leq t_\omega \leq t_0 \\ 0, & t_0 < t_\omega \end{cases} \quad (16'')$$

If the finiteness of the inlet sample volume is not important, then one can consider  $t_0 \rightarrow 0$  with  $C_0 t_0 = M$  (the initial condition is a delta-function) and the solution of the problem 16, 16'' takes the form<sup>8</sup> (see also ref. 10)

$$C'(x_\omega, t_\omega) = \frac{k_1}{2k_2} \sqrt{\frac{\tau}{k_1 x_\omega}} \cdot \frac{(e^R - 1) \exp \left[ -\frac{(t_\omega - k_1 x_\omega)^2}{4\tau k_1 x_\omega} \right]}{\sqrt{\pi} + (e^R - 1) \frac{\sqrt{\pi}}{2} \left[ 1 - \Phi \left( \frac{t_\omega - k_1 x_\omega}{\sqrt{4\tau k_1 x_\omega}} \right) \right]} \quad (17)$$

where  $R = k_2 C_0 t_0 / k_1 \tau$  is a measure of non-linearity and  $\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x d\xi \cdot \exp(-\xi^2)$ . Consequently, the solution  $C_\omega(x, t) = C'[x_\omega(x, t), t_\omega(x, t)]$  is a function of

$$x_\omega = \int_0^x d\xi \cdot \frac{\mu_\omega(\xi)}{w}, \quad t_\omega = t - \int_0^x d\xi \cdot \frac{\varepsilon_\omega(\xi)}{w}$$

*i.e.*, of integrals of the random processes  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$ . As above, the variance of the random quantity  $C_\omega(x, t)$  for  $x \gg \varrho$  [here  $\varrho = \max(\lambda_\varepsilon, \lambda_\mu)$  and  $\lambda_\varepsilon, \lambda_\mu$  are correlation lengths for the random processes  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$ ;  $\lambda_\varepsilon$  and  $\lambda_\mu$  are equal in order of magnitude to the mean radius of the particles of the bed] is given by the expression  $\mathcal{D}[C_\omega(x, t)] \approx x^{-1}$ . Consequently, variations of the random quantity  $C_\omega(x, t)$  with respect to its mean  $\langle C_\omega(x, t) \rangle$  are insignificant. This implies that, as in the previous section, for columns of length  $L \gg \varrho$  the eluted curve can be expressed as:

$$C_{\omega}(x = L, t) \stackrel{\text{Prob} = 1}{=} \langle C_{\omega}(x = L, t) \rangle \equiv \bar{C}(x = L, t)$$

As in the case of a linear isotherm, substitution of expressions 6 into expressions 15 yields:

$$C_{\omega}(x, t) = C' \left[ \frac{\mu_0}{w} \cdot x + \int_0^x d\xi \cdot \frac{\mu_{1,\omega}(\xi)}{w}, t - \frac{\varepsilon_0}{w} \cdot x - \int_0^x d\xi \cdot \frac{\varepsilon_{1,\omega}(\xi)}{w} \right] \quad (18)$$

The integrals of the random Gaussian processes

$$\hat{\varepsilon}_{\omega}(x) = \int_0^x d\xi \cdot \varepsilon_{1,\omega}(\xi), \hat{\mu}_{\omega}(x) = \int_0^x d\xi \cdot \mu_{1,\omega}(\xi)$$

are known (see ref. 5, Ch. 11) to be, in turn, Gaussian processes with zero means. Consequently, the average over realizations  $\omega \in \Omega$  for the function 18 has the form

$$\begin{aligned} \langle C_{\omega}(x, t) \rangle &= \\ &= \int_{-x}^{+x} d\eta_1 \int_{-x}^{+x} d\eta_2 C' \left( \frac{\mu_0}{w} \cdot x + \frac{\eta_1}{w}, t - \frac{\varepsilon_0}{w} \cdot x - \frac{\eta_2}{w} \right) \mathcal{W}_{\varepsilon,\mu}(\eta_1, \eta_2, x) \end{aligned} \quad (19)$$

where  $\mathcal{W}_{\varepsilon,\mu}(\eta_1, \eta_2, x)$  is the probability distribution density of the random quantities  $\hat{\varepsilon}_{\omega}(x)$  and  $\hat{\mu}_{\omega}(x)$  (the parameter  $x$  is fixed).

Let us first consider the case when the quantities  $\varepsilon_{\omega}(x)$  and  $\mu_{\omega}(x)$  are independent of each other. Then  $\mathcal{W}_{\varepsilon,\mu}(\eta_1, \eta_2, x)$  can be represented as a product of probability distribution densities which separately characterize each random quantity<sup>5</sup>:

$$\mathcal{W}_{\varepsilon,\mu}(\eta_1, \eta_2, x) = \mathcal{W}_{\varepsilon}(\eta_1, x) \mathcal{W}_{\mu}(\eta_2, x) \quad (20)$$

The probability distribution densities  $\mathcal{W}_{\varepsilon}$  and  $\mathcal{W}_{\mu}$  can be found as in the case of a linear isotherm. Consequently:

$$\mathcal{W}_{\varepsilon}(\eta, x) = \frac{1}{\sqrt{2\pi D_{\varepsilon} \dot{\lambda}_{\varepsilon} x}} \cdot \exp\left(-\frac{\eta^2}{2D_{\varepsilon} \dot{\lambda}_{\varepsilon} x}\right) \quad (21)$$

$$\mathcal{W}_{\mu}(\gamma, x) = \frac{1}{\sqrt{2\pi D_{\mu} \dot{\lambda}_{\mu} x}} \cdot \exp\left(-\frac{\gamma^2}{2D_{\mu} \dot{\lambda}_{\mu} x}\right) \quad (22)$$

Substituting the expressions 21 and 22 into relationship 19 yields:

$$\langle C_{\omega}(x, t) \rangle = \int_{-x}^{+x} d\eta \int_{-x}^{+x} d\gamma \cdot C' \left( \frac{\mu_0}{w} \cdot x + \frac{\eta}{w}, t - \frac{\varepsilon_0}{w} \cdot x - \frac{\gamma}{w} \right) \mathcal{W}_{\varepsilon}(\eta, x) \mathcal{W}_{\mu}(\gamma, x) \quad (23)$$



The analysis of expression 23 for the general solution 17 of the non-linear eqn. 14 is complicated. Numerical analysis of the expression 23 and its comparison with the solution when stochastic coefficients  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$  are assumed to be constant and equal to  $\varepsilon_0$  and  $\mu_0$  show that the effect of irregularity leads to dispersion of eluted peaks.

In an explicit form the effect of packing irregularity can be examined for two particular cases when expression 17 has a simpler form<sup>8,10</sup>.

(a) Let  $|R| \ll 1$  (small non-linearity) then expression 17 takes the form:

$$C'(x_\omega, t_\omega) = \frac{C_0 t_0}{\sqrt{4\pi\tau k_1 x_\omega}} \cdot \exp\left[-\frac{(t_\omega - k_1 x_\omega)^2}{4\tau k_1 x_\omega}\right] \quad (24)$$

Owing to the Gaussian property of the random process  $\mu_\omega(x)$ , for  $x \gg \lambda_\mu$  one obtains  $\hat{\mu}_\omega(x) \approx \sqrt{D_\mu \lambda_\mu x}$ . Therefore, expression 23, after substitution by eqn. 24, can be reduced (to first order in  $\varrho/x$ ) to the form

$$\langle C_\omega(x, t) \rangle = \frac{C_0 t_0 w}{\sqrt{\pi(4\tau k_1 w \mu_0 x + 2D_\varepsilon \lambda_\varepsilon x + 2D_\mu \lambda_\mu k_1^2 x)}} \times \quad (25)$$

$$\left[1 - A \cdot \frac{t w - (\varepsilon_0 + k_1 \mu_0) x}{x}\right] \times \exp\left\{-\frac{[t w - (\varepsilon_0 + k_1 \mu_0) x]^2}{4\tau k_1 w \mu_0 x + 2D_\varepsilon \lambda_\varepsilon x + 2D_\mu \lambda_\mu k_1^2 x}\right\}$$

where

$$A = \frac{4\tau k_1^2 w D_\mu \lambda_\mu}{(4\tau k_1 w \mu_0 + 2D_\varepsilon \lambda_\varepsilon + 2D_\mu \lambda_\mu k_1^2)}$$

Hence it follows that, first, the dispersion of an eluted peak increases if irregularity in both parameters  $\varepsilon_\omega(x)$  and  $\mu_\omega(x)$  has been taken into account. Secondly, the outlet curve becomes slightly asymmetric even for a linear isotherm.

(b) For the case of  $|R| \gg 1$  (high non-linearity) and  $k_2 \geq 0$  (the case of  $k_2 \leq 0$  is treated analogously, see refs. 8, 10) we obtain:

$$C'(x_\omega, t_\omega) = \begin{cases} \frac{t_\omega - k_1 x_\omega}{2k_2 x_\omega}, & 0 \leq t_\omega - k_1 x_\omega \leq \sqrt{4R\tau k_1 x_\mu} \\ 0, & \text{for other values of the argument} \end{cases} \quad (26)$$

Then

$$\langle C_\omega(x, t) \rangle = \frac{1}{2k_2 \mu_0 x} \cdot \int_{-x}^{+x} d\gamma \cdot \mathcal{W}_\mu(\gamma, x) \times \left\{ \frac{B_1}{2} \left[ \Phi\left(\frac{B_1}{\sqrt{2D_\varepsilon \lambda_\varepsilon x}}\right) - \Phi\left(\frac{B_1 - B_2}{\sqrt{2D_\varepsilon \lambda_\varepsilon x}}\right) \right] + \right.$$

$$+ \frac{\sqrt{D_\varepsilon \lambda_\varepsilon x}}{\sqrt{2\pi}} \left[ \exp\left(-\frac{B_1^2}{2D_\varepsilon \lambda_\varepsilon x}\right) - \exp\left(-\frac{(B_1 - B_2)^2}{2D_\varepsilon \lambda_\varepsilon x}\right) \right] \Bigg\}$$

where  $B_1 = tw - (\varepsilon_0 + k\mu_0)x - k_1\gamma$  and  $B_2 = \sqrt{4k_2 C_0 t_0 \mu_0 w x}$  for the case  $x \gg \varrho$ . Analysis of expression 27 reveals that a shock-wave type solution of eqn. 26 (resulting in the absence of packing irregularity<sup>8,10</sup>) is smeared out if the irregularity is taken into account, because now this solution convolutes with two Gaussian distributions.

Let us consider another case when  $\varepsilon$  and  $\mu$  are linearly connected (see first section), or  $\mu = (1 - \varepsilon)n$ . In this case the solution of eqn. 14 has a form analogous to 17 where:

$$x_\omega = \frac{nx}{w} - \frac{n}{w} \int_0^x d\xi \cdot \varepsilon_\omega(\xi), \quad t_\omega = t - \frac{1}{w} \int_0^x d\xi \cdot \varepsilon_\omega(\xi) \quad (28)$$

Following the same reasoning as in the case of independent  $\varepsilon$  and  $\mu$ , let us represent the random process  $\varepsilon_\omega(x)$  in the form  $\varepsilon_\omega(x) = \varepsilon_0 + \varepsilon_{1,\omega}(x)$  where  $\varepsilon_{1,\omega}(x)$  is a stationary

Gaussian random process of the Markov type with a zero mean. Let  $\hat{\varepsilon}_\omega(x) = \int_0^x d\xi \cdot \varepsilon_{1,\omega}(\xi)$ . Then

$$\langle C_\omega(x, t) \rangle = \int_{-\infty}^{+\infty} d\hat{\varepsilon} \cdot \mathcal{W}(\hat{\varepsilon}, x) C'(x_\omega, t_\omega) \quad (29)$$

where  $\mathcal{W}(\hat{\varepsilon}, x)$  is the probability distribution density of the random quantity  $\hat{\varepsilon}_\omega(x)$  (the parameter  $x$  is fixed). Because the process  $\varepsilon_{1,\omega}(x)$  is Gaussian, stationary and Markovian, then for  $x \gg \lambda$  ( $\lambda$  being the correlation length),  $\mathcal{W}(\hat{\varepsilon}, x)$  has the form:

$$\mathcal{W}(\hat{\varepsilon}, x) = \frac{\exp\left(-\frac{\hat{\varepsilon}^2}{2D_\varepsilon \lambda_\varepsilon x}\right)}{\sqrt{2\pi D_\varepsilon \lambda_\varepsilon x}} \quad (30)$$

As above, expression 29 can be studied for two extreme ranges of the non-linearity parameter  $R$ .

(a) Let  $|R| \ll 1$ ; then to first order in  $\lambda_\varepsilon/x$  one obtains:

$$\langle C_\omega(x, t) \rangle = \frac{C_0 t_0 w}{\sqrt{\pi[4\tau k_1 w \mu_0 x + 2D_\varepsilon \lambda_\varepsilon x (1 - nk_1)^2]}} \times$$

$$\exp \left\{ - \frac{[tw - (\varepsilon_0 + k_1\mu_0)x]^2}{4\tau k_1 w \mu_0 x + 2D_\varepsilon \lambda_\varepsilon x (1 - nk_1)^2} \right\}$$

(b) If  $|R| \gg 1$ , then

$$\begin{aligned} \langle C_\omega(x, t) \rangle &= \frac{A}{4n(1 - \varepsilon_0) k_2 x} \left[ \Phi \left( \frac{\alpha A}{\sqrt{2D_\varepsilon \lambda_\varepsilon x}} \right) - \Phi \left( \frac{\alpha A - \alpha B}{\sqrt{2D_\varepsilon \lambda_\varepsilon x}} \right) \right] + \\ &+ \frac{(1 - k_1 n) \sqrt{D_\varepsilon \lambda_\varepsilon x}}{2k_2 n(1 - \varepsilon_0)} \left\{ \frac{1}{\sqrt{2\pi}} \times \exp \left[ - \frac{(\alpha A)^2}{2D_\varepsilon \lambda_\varepsilon x} \right] - \frac{1}{\sqrt{2\pi}} \cdot \exp \left[ - \frac{(\alpha A - \alpha B)^2}{2D_\varepsilon \lambda_\varepsilon x} \right] \right\} \end{aligned}$$

where

$$\begin{aligned} A &= t - \frac{\varepsilon_0(1 - k_1 n) + k_1 n}{w} \cdot x, \\ B &= \sqrt{\frac{4k_2 C_0 t_0 n (1 - \varepsilon_0) x}{w}}, \quad \alpha = \frac{w}{1 - k_1 n} \end{aligned}$$

This analysis demonstrates that random variations of  $\varepsilon$  and  $\mu$  along the bed length result in an additional broadening of the eluted sample peak also in the case of a non-linear isotherm.

#### *Phenomenological consequences of packing irregularity*

Let us consider again the case of a linear isotherm in the theory of ideal sorption dynamics or chromatography. The effect of packing irregularity can be examined either by solving eqn. 3 with subsequent averaging of  $C_\omega(x, t)$  over all realizations of the packing  $\Omega$ , or by solving the sorption dynamics equation for an observable mean concentration,  $\bar{C}(x, t)$ , where irregularity is taken into account by an additional "diffusion-type" term (see eqn. 11). It should be noted that the sorption dynamics equation is usually solved by using the following mean field approximation for the average of the product of two random quantities:

$$\langle [\varepsilon_\omega(x) + k\mu_\omega(x)] \hat{c}_i C_\omega \rangle \approx \langle \varepsilon_\omega(x) + k\mu_\omega(x) \rangle \hat{c}_i \langle C_\omega \rangle = (\varepsilon_0 + k\mu_0) \hat{c}_i \bar{C}$$

In this approximation eqn. 3 reduces to the form (compare eqn. 11)

$$(\varepsilon_0 + k\mu_0) \hat{c}_i \bar{C} + w \hat{c}_x \bar{C} = 0 \quad (31)$$

whose solution under conditions 2 is the "running wave"

$$\bar{C}(x, t) = f \left( t - \frac{\varepsilon_0 + k\mu_0}{w} \cdot x \right)$$

which is different from the solution 10 *i.e.*, the effect of packing irregularity is lost in this approximation.

Differentiating expression 10 with respect to  $x$  and using  $\partial_x \mathcal{W}_v = \frac{D\lambda}{2} \cdot \partial_\eta^2 \mathcal{W}$ , we obtain an equation for the function  $\bar{C}(x, t)$  (see also eqn. 11):

$$(\varepsilon_0 + k\mu_0) \partial_t \bar{C} + w \partial_x \bar{C} = \frac{D\lambda}{2w} \cdot \partial_t^2 \bar{C} \quad (32)$$

In contrast to eqn. 31, eqn. 32 has a non-trivial right-hand term which results in peak broadening if there is no longitudinal diffusion. Eqn. 32 is in accord with the phenomenological retardation-time concept mentioned above (see also Appendix and refs. 7-9).

As noted in the previous section, see eqn. 14, the sorption dynamics equation in the theory of non-ideal chromatography with a linear isotherm has the form:

$$[\varepsilon_\omega(x) + k_1 \mu_\omega(x)] \partial_t C_\omega + w \partial_x C_\omega = k_1 \tau \mu_\omega(x) \partial_t^2 C_\omega \quad (33)$$

Then, similarly to the derivation of eqn. 32, we obtain:

$$(\varepsilon_0 + k_1 \mu_0) \partial_t \bar{C} + w \partial_x \bar{C} = k_1 \tau \langle \mu_\omega(x) \partial_t^2 C_\omega \rangle + \frac{D\lambda}{2w} \cdot \partial_t^2 \bar{C} \quad (34)$$

Let us the approximation  $\langle \mu_\omega \partial_t^2 C_\omega \rangle \approx \mu_0 \partial_t^2 \bar{C}$ . Then the effect of irregularity in the packed bed can be taken into consideration in the framework of the retardation-time model by introducing the phenomenological coefficient  $\tau_{\text{eff}} = \tau + \tau^*$  (*cf.*, eqn. 34)

$$(\varepsilon_0 + k_1 \mu_0) \partial_t \bar{C} + w \partial_x \bar{C} = k_1 \mu_0 \tau_{\text{eff}} \partial_t^2 \bar{C}$$

where for  $\tau^*$  and  $\tau$  we have obtained explicit expressions, see eqns. 12 and A3.

Using these expressions we can evaluate the contribution of the effect of packing irregularity to the total peak dispersion. For example, a typical value of the time  $\tau$  in gas-liquid chromatography (see eqn. A3 and ref. 1) is about  $10^{-5}$  sec. From ref. 3, the characteristics of a packed bed are  $\Delta = \sqrt{D_p/\varepsilon_0} \approx 0.2$  for  $\varepsilon_0 = 0.4$  when the ratio of the column diameter to the particle diameter,  $\zeta = d/2r = 16$ . Then for ordinary sorption dynamics conditions  $w = 10$  cm/sec,  $\mu_0 k_1 = 10$  and correlation length  $\lambda \approx 4r = 0.1$  cm, we obtain from eqn. 11:

$$\tau^* \approx 0.32 \cdot 10^{-5} \text{ sec} \quad (36)$$

As observed in ref. 3, the parameter  $\Delta$  regularly decreases with increasing  $\zeta$ . Therefore, the ratio  $\tau^*/\tau$  is allowed to vary from several per cent to several tens of per cent for small  $\zeta$ .

## CONCLUSIONS

The importance of non-kinetic sources for chromatographic peak broadening upon migration through a granular medium was pointed out in ref. 11. But it was

Giddings who examined this question systematically and proposed clear concepts for evaluating this bed packing effect, see ref. 1 for a review and references.

The main important difference between that work and our theory can be summarized as follows. Radushkevich<sup>11</sup> and Giddings<sup>1</sup> reduced the packing irregularity effect to a diffusion process (eddy diffusion, see ref. 1, Chs. 2 and 5) which is responsible for additional zone dispersion in columns. In contrast, we have rigorously demonstrated that the bed packing irregularity:

(i) can be reduced to a kinetic process, corresponding to the retardation-time concept

(ii) causes asymmetry of the eluted peak even for a linear sorption isotherm

Our approach allows one to understand some other types of bed irregularity in chromatography, *e.g.* surface films on stationary phases in open tubular columns.

## APPENDIX

### *Retardation-time concept for description of sorption-desorption kinetics*

In the present paper the packing irregularity effect is considered in the framework of retardation time concept in which non-ideality of the sorption dynamics (kinetics) is taken into account through a phenomenological time parameter,  $\tau$ . This time corresponds to the retardation of a sample distribution in the stationary phase with respect to that in a mobile phase. As shown in ref. 8 (see also ref. 9), for times greater than that for diffusion of a component in the liquid film of the stationary phase, this phenomenological concept is a rigorous consequence of a well-known exact system of equations describing the gas-liquid dynamics of sorption (see, *e.g.*, ref. 12):

$$\begin{aligned} \hat{c}_t a &= \mathcal{D}_t \hat{c}_y^2 a, \\ \varepsilon \hat{c}_t C + w \hat{c}_x C &= s \mathcal{D}_1 \hat{c}_y a(x, y = 0, t) \\ \hat{c}_y a(x, y = h, t) &= 0 \end{aligned} \quad (\text{A1})$$

Here  $a = a(x, y, t)$  is a solute concentration in the stationary phase,  $C = C(x, t)$  a solute concentration in the mobile phase,  $y$  a coordinate inside the stationary phase film ( $h =$  film thickness),  $\mathcal{D}_1$  is the diffusion coefficient in the liquid film of the stationary phase,  $\mathcal{D}_t$  is the longitudinal coefficient, and  $S$  is the specific area of the surface boundary between phases (per unit column length and per unit column cross-section).

*Proposition (see refs. 8 and 9).* For  $\mathcal{D}_t \gg h^2$  the system of equations A1 is equivalent to the following equation for the sorption dynamics

$$\varepsilon \hat{c}_t C(x, t) + k_1 \mu \hat{c}_t a(x, y = 0, t) + w \hat{c}_x C(x, t) = \tau \mu k_1 \hat{c}_t^2 C(x, t) \quad (\text{A2})$$

where  $\mu = sh$  and  $a(x, y = 0, t) = k_1 C(x, t) + \dots$ . For the retardation-time parameter one obtains:

$$\tau = h^2 / 3 \mathcal{D}_t \quad (\text{A3})$$

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